

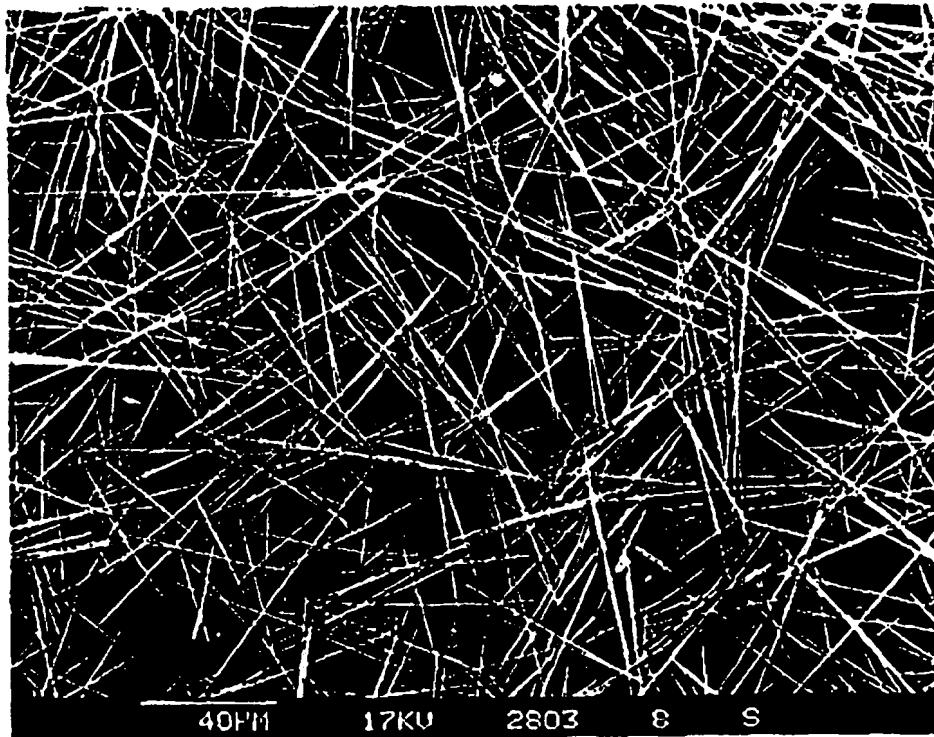


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: FIBROUS SILICATE HYDRATES AND PROCESSES FOR THEIR PRODUCTION

(57) Abstract

A method for the production of discrete fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates of predetermined average fibre length comprising mixing an aqueous solution of a soluble calcium salt with a soluble silica source and heating the mixture to form the fibrous product.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Fibrous Silicate Hydrates and Processes for Their Production

The invention relates to a process for the production of fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates and to such fibrous compounds produced thereby.

Background Art

Suitable materials have been sought as replacements for asbestos fibres for reinforcement in composites such as cement/fibre board. Use as a reinforcement is not limited to such composites however, as many polymer materials require reinforcing and fibres of varying lengths are required in such areas. When used in cementitious products such fibres need to be strong and compatible with the highly alkaline pore fluids of cement binding systems. Asbestos fibres initially proved suitable, being chemically inert and also able to withstand elevated temperatures. Asbestos is a generic name for a series of magnesium silicates which occur naturally as long fibres. However, use of asbestos is generally no longer acceptable due to the health problems that may result. Glass fibres have also been used as reinforcement in cement composites but these are attacked by the alkaline pore solution and dissolve or become brittle, losing their ability to act as reinforcement fibres. Cellulose fibres have also been used as these are not a biological hazard but these fibres are not alkali stable and slowly become brittle in the alkaline environment. The composite material formed from such fibres will therefore also lose flexural strength and become brittle. Calcium silicate minerals can occur naturally as fibres, and compounds such as Xonotlite and Wollastonite have been trialled in cement composites. However, the length of the fibres in these naturally occurring minerals is short and enhancement in flexural properties is limited. Further, in general the naturally occurring fibres are not in discrete form but rather form clumps of fibres. For use as

reinforcement it is very advantageous that fibres be discrete in order that an even distribution of the fibres is possible within the base material to gain the maximum effect on flexural properties.

One example of a fibrous material used as a reinforcing fibre in polymers is the ceramic Barium titanate. However this is expensive to manufacture and requires grinding down to suitable length for use in many cases. Toxicity of this material can also be a problem as the body is unable to dissolve or otherwise eliminate ceramic fibres.

In the past calcium silicate hydrates have been formed from calcium silicate compounds which are prepared in cement kilns at elevated temperatures. These compounds are then hydrated with water to form the calcium silicate hydrates. At normal conditions, the product of this hydration is an amorphous calcium silicate hydrate, which is suitable for use as a binder. If the curing temperature is raised, such as in an autoclave or geothermal well, crystalline calcium silicate hydrates can be formed. It is also known that crystalline calcium silicate hydrates can be formed from insoluble calcium compounds, such as calcium hydroxide, by preparing an aqueous slurry with an insoluble silicate material, such as quartz, and heating the aqueous calcium silicate gel formed in the slurry above the boiling point of water. The nature of the product formed is dependent on the Ca:Si ratio. Typical products formed at high Ca:Si ratios include tricalcium silicate hydrate (Ca:Si = 3) and dicalcium silicate hydrate (Ca:Si = 2). These materials do not contain silicate chains in their structure and are therefore not suitable as materials for forming calcium silicate hydrate fibres. Fibrous calcium silicate hydrates can be formed at low Ca:Si ratios around Ca:Si = 1 however. For example Tobermorite (Ca:Si = 0.85) and Xonotlite (Ca:Si = 1) are two such compounds.

The manufacture of synthetic calcium silicate fibres is known, however in general only clumps of fibres have been able to be formed. Where discrete fibres have been formed there has been no disclosure of how this discrete form can be effectively reproduced. Further, there has been no disclosure of a method wherein discrete fibres can be formulated of a targeted predetermined length.

The ability to combine these two factors is of significant commercial importance as fibre length and discreteness are important when considering reinforcement of materials and in particular polymeric materials.

United States Patent 4,277,457 to Tokuyama Soda Kabushiki Kaisha, inventors Genji Toga et al, discloses the manufacture of a novel alkali calcium silicate from an aqueous suspension of SiO_2 , Ca, and alkali, under specific reaction conditions. There is disclosure of the use of soluble starting components however, in general, the starting mixture is a suspension. It is notable that insoluble starting components may be used. Further, the ratio of components in the starting mixture is not considered important. This is reflected by the allowance of the use of suspensions as the starting mixture. There is therefore no teaching of the necessity to have a starting solution with specific component ratios in order to create discrete fibres and there is also no teaching of how fibres of a known average length may be formed. Further, use of such suspensions is likely to require the use of abrasion resistant equipment over the longer term.

It is an object of this invention to provide a method of preparing fibrous calcium silicate hydrates as well as sodium calcium silicate hydrates as discrete fibres and of predetermined fibre length.

Summary of the Invention

The invention comprises a method for the production of discrete fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates of predetermined average fibre length comprising mixing an aqueous solution of a soluble calcium salt with a soluble silica source and heating the mixture to form the fibrous product.

The invention further comprises a method for preparing discrete calcium silicate fibres of predetermined average length by

- (a) preparing an aqueous gel solution of a soluble calcium salt and a soluble silica source having a specific molar ratio of calcium:silica effective to produce predetermined fibrous calcium silicate hydrates and/or sodium silicate hydrates;
- (b) heating the aqueous gel solution to a temperature and for a time effective to produce the predetermined fibrous hydrates at said predetermined length; and
- (c) recovering the product.

Preferably the calcium silicate fibres formed comprise a mixture of fibrous calcium silicate compounds.

Preferably the product contains a mixture of Pectolite and tricalcium silicate hydrate fibres.

Preferably the temperatures used are between about 140°C and about 400°C.

Preferably the temperature used is between 170°C and 360°C and more preferably between 250 and 300°C.

Preferably the fibre length produced is between about 1 μm and about 500 μm .

Preferably the fibre length is between 2 and 300 μm and more preferably between 2 and 200 μm .

Preferably the Ca:Si molar ratios are between 0.2 and 5.0 and more preferably between 0.5 and 2.5.

The invention further comprises a method for the preparation of discrete calcium silicate fibres including the sodium calcium silicate hydrate Pectolite comprising mixing a soluble calcium salt with a soluble silica source and a soluble sodium salt in a Ca:Si ratio of from about 0.20 to about 0.76 and heating the mixture to a temperature of between about 200°C and about 365°C, to obtain discrete fibres having a length of between about 25 and about 60 μm .

Preferably the Ca:Si ratio is between 0.25 to 0.65, the temperature is between 250 and 300°C and the fibre length is between 25 and 50 μm .

Preferably the soluble silica source and the soluble sodium salt are both sodium silicate.

Preferably the soluble sodium source includes additional NaOH.

The invention further comprises a method for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate Tobermorite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 0.45 to about 2.0 and heating the

mixture to a temperature of between about 150°C and about 305°C, to obtain discrete fibres having a length between about 1 and about 15 μm .

Preferably the Ca:Si ratio is between 0.5 and 1.5, the temperature is between 175 and 275°C and the fibre length is between 2 and 10 μm .

The invention further comprises a method for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate Xonotlite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 0.8 to about 5.0 and heating the mixture to a temperature of between about 250°C and about 320°C, to obtain discrete fibres having a length of between about 2 and about 15 μm .

Preferably the Ca:Si ratio is between 1 and 3.0, the temperature is between 275 and 300°C and the fibre length is between 4 and 10 μm .

The invention further comprises a method for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate Foshagite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 0.80 to about 1.60 and heating the mixture to a temperature of between about 235°C and about 315°C, to obtain discrete fibres having a length of between about 15 and about 40 μm .

Preferably the Ca:Si ratio is between 1 and 1.5, the temperature is between 250 and 300°C and the fibre length is between 15 and 30 μm .

The invention further comprises a method for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate Hillebrandite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 1.67 to about 2.50 and heating the mixture to a temperature of between about 235°C and about 370°C, to obtain discrete fibres having a length of between about 10 and about 55 μm .

Preferably the Ca:Si ratio is between 1.9 and 2.3, the temperature is between 245 and 360°C and the fibre length is between 10 and 40 μm .

Preferably the fibres produced have a fibre length having a percentage standard deviation of less than about 45% and more preferably less than about 35%.

Preferably the mixture is heated for between about 1 and about 6 hours and more preferably between about 2 and about 5 hours.

Preferably the solutions are heated in a sealed vessel.

Preferably the soluble calcium salt is calcium nitrate or calcium chloride.

Preferably the soluble silica source is an alkaline silicate.

Preferably the soluble silica source is sodium silicate.

Preferably the calcium salt solution is premixed with the soluble silica source and then heated to form the fibrous material.

Preferably the soluble silica source is in aqueous solution.

Preferably the soluble silica solution is preheated in a sealed vessel and the soluble calcium salt solution is pumped into the vessel.

Preferably additional sodium hydroxide is added to the silicate solution in a concentration appropriate for the desired product.

Preferably additional potassium hydroxide is added to the silicate solution.

Preferably the soluble silica solution and the soluble calcium salt solution are pumped separately into a preheated sealed vessel.

Preferably the sealed vessel is an autoclave.

Drawings

The attached Figures show X-ray diffraction patterns and scanning electron microscope results of fibrous calcium silicate hydrates formed by the method of the invention. In the Figures:

Fig 1a shows a comparison between the X-ray diffraction pattern for the product formed by the process of Example 1 and a standard Pectolite pattern;

Figs 1b and 1c shows a scanning electron microscope picture of Pectolite produced by process of the invention;

Fig 1d shows a scanning electron microscope picture of Pectolite forming from Tobermorite produced by process of the invention;

Fig 2a shows a comparison between the X-ray diffraction pattern for the product formed by the process of Example 2 and a standard Tobermorite pattern;

Fig 2b shows a scanning electron microscope picture of Tobermorite produced by process of the invention;

Fig 3a shows a comparison between the X-ray diffraction pattern for the product formed by the process of Example 3 and a standard Xonotlite pattern;

Fig 3b shows a scanning electron microscope picture of Xonotlite plus some Foshagite produced by process of the invention;

Fig 4a shows a comparison between the X-ray diffraction pattern for the product formed by the process of Example 4 and a standard Foshagite pattern;

Fig 4b shows a scanning electron microscope picture of Foshagite produced by the process of the invention;

Fig 5a shows a comparison between the X-ray diffraction pattern for the product formed by the process of Example 5 and a standard Hillebrandite pattern;

Fig 5b shows a scanning electron microscope picture of Hillebrandite produced by the process of the invention.

Fig 6 shows a photomicrograph of the product of Example 8a.

Fig 7 shows a photomicrograph of the product of Example 8b.

Fig 8 shows a photomicrograph of the product of Example 8c.

Fig 9 shows a photomicrograph of the product of Example 8d.

Figs 10 to 21 show photomicrographs of the products of Examples 9 to 20 respectively.

Detailed Description of the Invention

The invention relates to a method for production of discrete fibres of a predetermined or targeted average length including fibrous calcium silicate hydrates or sodium calcium silicate hydrates from a starting solution. The solution produced will be in gel form due to the presence of the soluble silica source. The use of a solution as the starting mixture allows a precise starting component ratio to be used and removes the need for specialised abrasion resistant equipment such as pumps and the like.

(1) Obtaining Discrete Fibres

A soluble calcium salt can be mixed with a soluble silica source giving an alkaline solution containing a homogenous gel of calcium ions and silicate ions and/or sodium ions. These can be premixed and transferred to an autoclave or premixed in an autoclave by carefully adding

the calcium salt solution to the alkaline sodium silicate solution, and then holding at the desired temperature. This results in the growth of crystals having a discrete elongate structure. By starting with a solution containing the required starting components and following the general process steps as described, discrete fibres are obtained.

One preferred method involves the soluble calcium salt solution being slowly pumped under pressure into the alkaline sodium silicate solution which is held at temperature and pressure in a sealed autoclave. This gives excellent fibre separation. As will be apparent, heating the silicate solution in a sealed vessel will result in an internal pressure in the vessel (ie an autogenous pressure). It is as a result of this pressure that the calcium solution must be pumped into the vessel. The internal pressure, and thus the required pumping pressure, will be dependant on the temperature to which the vessel is heated and on the volume of the vessel used. This temperature, pressure and volume relationship will be well known to a person skilled in the art.

Another preferred method is to preheat the autoclave, or other suitable vessel, to the desired temperature and then pump the two solutions simultaneously into the autoclave. This will tend to produce larger fibres. Again, due to the internal pressure in the autoclave, the solutions must be pumped in.

(2) Obtaining Desired Fibre Lengths

The temperature to which the mixture/vessel is heated is preferably in excess of 140°C however, as will be described in more detail hereinafter, specific temperature ranges will preferably be used to result in specific fibrous crystalline products. In this way predetermined fibre lengths within acceptable commercial bounds can be obtained as desired. The preferred

device used to heat the mixture is a sealed autoclave, although any suitable device as will be known in the art may be used, e.g. a tubular reactor. The temperatures selected and the time for which the mixture is heated is critical to obtain the desired length of fibre. The combination of specific component ratios and heating temperatures and times gives predictable products of standard length. It is a simple matter of optimisation of the process parameters, as will be readily apparent to a skilled person which is required in order to obtain predetermined fibre length within acceptable commercial bounds. Thus if the component ratio in the starting solution is consistent with Pectolite production fibre lengths within the Pectolite standard range will be formed and longer or shorter lengths can be obtained by varying the temperature of production appropriately. If shorter lengths of Pectolite fibres are needed, it is probable that a combination of Pectolite and Foshagite will be obtained as a mixture of long Foshagite fibres and short Pectolite fibres. Other compound relationships as will be known in the art can also be obtained. It is notable that by using the process of the invention with high temperatures, high alkalinity, and high Ca:Si ratio (about 3), tricalcium silicate hydrate fibres can be formed. These fibres tend to be long however they are also relatively unstable.

For example at temperatures around 150°C, and Ca:Si ratio 0.5-1.4, Tobermorite is formed; at higher temperatures, approximately 180°C to 300°C, Xonotlite is synthesised.

If extra sodium hydroxide is added to the sodium silicate solution and the reaction is carried out at approximately 300°C, the mineral formed is Pectolite, a sodium calcium silicate. By varying the Ca:Si ratio as well as the Na:Si ratio other calcium silicate hydrates can be formed. The temperature of reaction time of exposure and component ratios therefore define the crystalline phases formed and the size of the fibres.

There is also a pH effect on the length and aspect ratio of the fibres produced by the process of the invention. At higher pH's the fibres tend to be longer and thinner, while at lower pH's the fibres tend to be shorter and wider. This pH effect is a function of the starting component ratios and can be regulated accordingly. Thus by manipulating the starting ratios and the temperatures specific control over fibre length is obtainable. In this way, when preparing longer Pectolite fibres, a starting mixture suitable for Pectolite and containing additional NaOH can produce a product having fibre lengths of about 60 μm and up to about 80 μm . Lengths up to 100 μm have been observed however these tend to be isolated fibres. KOH may also be used if desired.

Tobermorite, Pectolite, Xonotlite and the other phases able to be formed, crystallise as fibrous crystals. They have also been formed in Ordinary Portland Cement (OPC) systems heated to high temperatures. When formed in a binder in (OPC) systems with additional silica or sodium silicate, they give strength to composite products by the interlocking of their fibres. These crystalline compounds are composed of long silicate chains of silicate tetrahedra and form in strongly alkaline solutions, so will be stable in the alkaline pore fluid of cement paste. The longer and more discrete the fibres are the better the strength that will be imparted to the product. The fibres are also useful for reinforcing, and may be used primarily with polymer products. Shorter fibre lengths are generally suitable in these cases and, provided the fibres are discrete, excellent strength is imparted. Examples of such polymers are epoxy and polyester resins which contain oxygen and which will bond strongly with the hydroxyl groups present on the silica chains of the fibres.

The time at temperature must be sufficient to form the product. A formulation designed to prepare Pectolite will form only Tobermorite if the combination of temperature and time are

decreased sufficiently. At intermediate temperature and time, a combination of Tobermorite and Pectolite will result. Thus if the fibre length required falls approximately on the Pectolite/Tobermorite boundary a combination of these compounds will be present in the product formed. The Pectolite/Tobermorite example is one of the more unlikely combinations when seeking standard fibre lengths however, as this is a combination of large (Pectolite) and small (Tobermorite) fibres. Better examples when seeking standard fibre lengths, would be Pectolite/Foshagite, Pectolite/Xonotlite, Foshagite/Xonotlite, Foshagite/Hillebrandite. The time used will be a function of the temperature and is generally between 1 and 6 hours. Between 2 and 5 hours at temperature is generally sufficient.

The calcium salts useful in the method may be any of the soluble calcium salts as will be well known in the art although calcium nitrate and calcium chloride are preferred. The silicates may also be any of the soluble silicates as will be known in the art however the alkaline silicates, and in particular sodium silicate, are preferred. Solutions are used as they facilitate the formation of discrete fibres. Further, the necessity for abrasion resistant pumps and the like is removed when solutions are used. Previous workers have used solid state reactions and have started with suspensions and like compositions however these have the inherent disadvantage of abrasion and also generally need longer reaction times to obtain a suitable product.

As will be readily apparent from the following examples, by controlling the component ratio in the starting solution known forms of silicate fibres are obtained. By following the precise process conditions discrete fibres are obtained. As the varying forms of silicate fibres have varying lengths, the length of fibres can be selected within a very precise range. By varying the temperature used in the process, in combination with the ratio of the starting components

in solution, specific fibre lengths can be selected. As mentioned previously this may result in mixtures of silicate compounds, however the length of those fibres will be very similar and within acceptable commercial bounds. As the starting material is a solution the component content can be precisely controlled giving excellent quality control over the final product. The percentage standard deviations of the fibre lengths produced can be as low as 45% and lower figures such as 35%, are achievable. It is envisaged that with the more precise control obtainable in the commercial arena repeatable quantities of fibres having percentage standard deviations as low as 20% will be possible. The combination of this length specificity with the ability to reliably produce discrete fibres makes the process of the present invention of significant commercial importance.

EXAMPLES

Specific methods (examples) for production of fibre types by pure batch (i.e. unpumped) method

Experiment required:

Hydrothermal reaction vessel: for large quantities, a stainless steel vessel should not be used, as all steels used in caustic solutions are subject to stress corrosion cracking (SSC) at temperatures above approx. 95°C, which can result in catastrophic failure. A vessel machined from or completely lined with monel 400 ($\frac{2}{3}$ Ni, $\frac{1}{3}$ Cu) alloy or nickel is suitable. For small quantities, we have found that small (25ml) capacity 316 stainless steel bombs with a PTFE seal, clamped in a galvanised steel frame are suitable. These are thick-walled and therefore lightly stressed. The bomb and frame is placed in a suitable fan oven.

Example 1

Pectolite ($\text{NaCa}_2\text{HSi}_3\text{O}_9$, PDF 33-1223) Ca:Si preferred initial ratio = 0.50 to 0.60.

Dissolve together:

0.100 mole (21.21g) of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and 0.30 mole (12.0g) of sodium hydroxide (NaOH) in distilled water and make up to 650g solution = (Si + NaOH) solution.

Dissolve 0.050 mole (11.81g) of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in distilled water and make up to 325g = Ca solution.

With vigorous stirring, slowly add the Ca solution (over approximately 1 minute) to the (Si + NaOH) solution to produce a white slurry with $[\text{Ca}]:[\text{Si}]:[\text{Na}] = 0.5:1:5$. Transfer this slurry to a suitable hydrothermal reaction vessel, rinse in with 25ml distilled H_2O to total 1000g mixture. Seal and heat to 300°C for soak time of 4 hours. Cool, open and remove contents.

Filter and wash with distilled water by a suitable method (e.g. mix with approximately 3 litres, allow to settle, decant liquid, repeat, then finally filter and rinse. Any suitable combination of dilution, decanting, centrifugation and/or filtration with washing to remove the unwanted NaOH and excess sodium metasilicate will suffice). After washing, the product can be dried and analysed by XRD. Unless the sample is ground well to break down fibres, an unusual XRD pattern is likely to result. To examine fibre morphology SEM is used. A drop of diluted slurry is placed on a glass slide mounted on an SEM stub and allowed to air-dry. Oven-drying tends to cause the fibres to clump together while drying.

Process tolerance:

The fibre morphology varies according to the reagent concentrations used. The ratio of Ca:Si used is preferably varied from less than 0.25 to approximately 0.65 but if raised too far may result in a mixture of phases, e.g. Pectolite plus ite. The NaOH concentration can vary by large factors. A higher concentration tends to result in larger fibres but can cause corrosion of the reaction vessel.

Temperature, and time at max temperature can be from approximately ≥ 4 hours at 250°C to ≥ 20 minutes at $\geq 350^\circ\text{C}$, to several days at 200°C. Variations in fibre size and morphology will depend on conditions. Generally, highest quality and size of fibres from a simple batch run will result from a moderate concentration of Si and Ca, combined with high NaOH concentrations and temperature.

Other phases:

Other phases, such as Xonotlite, Tobermorite, Foshagite and Hillebrandite can be produced using the same general method and reagents described for Example 1 by changing the ratios of reagents, temperature of reaction, time at temperature or replacing sodium hydroxide with potassium hydroxide. Using KOH will result in Tobermorite being formed, instead of Pectolite (Ref prep HFP 241).

Example 2

Tobermorite $(Ca_5(OH)_2Si_6O_{16} \cdot 4H_2O$; PDF 19-1364) Ca:Si starting ratio = 0.50.

When making Pectolite by the process of Example 1, Tobermorite is initially formed as the mixture heats up. If the maximum temperature and time are limited to less than approximately 240°C and 3-4 hours, then pure Tobermorite will result. Fibres of Tobermorite are very difficult to vacuum filter as they are extremely fine. However, they can be washed slowly by decantation and/or gravity filtering). At temperatures above 250°C, much larger Pectolite fibres begin to form until all of the Tobermorite is consumed.

Example 3

Xonotlite $(Ca_6(Si_6O_{17})OH_2$ PDF 29-379) Ca:Si preferred starting ratio = 1.0.

This is formed under similar temperature and time conditions to Pectolite, but requires an initial Ca:Si ratio of approximately 1:1 and much lower levels of NaOH concentration. Unless NaOH content is very low ($\approx 0.02M$) the Xonotlite product will usually contain some Foshagite or Pectolite.

Example 4

Foshagite $(Ca_4(SiO_3)_3(OH)_2$ PDF 29-377) Ca:Si starting ratio = 1.0.

This compound is made under the same temperature and time conditions as Pectolite in Example 1, except that Ca:Si = 1.0-1.33. Solution conditions require sufficiently high pH to prevent formation of Xonotlite. This is obtained by adding sufficient NaOH so the preferred concentration of NaOH is $\approx 0.1-1.0$ mole/litre.

Example 5

Hillebrandite $(Ca_2SiO_3(OH)_2$ PDF 9-51) Preferred Ca:Si starting ratio = 2.0.

NaOH concentration approximately 0.1M to $\geq 1.0M$.

Method for making Calcium Silicate-based Ceramic Fibres using Pumped Solutions (semi-batch process)***Equipment***

- Autoclave resistant to stress-corrosion cracking (e.g. Monel 400 alloy) suitable for operation at temperatures of at least 250°C and at corresponding hydrothermal pressures (>1000 psi) The particular equipment and conditions used in the following Examples were pumps No. 1 and No. 2 - 21 Monel autoclave rated at 4400 psi at 343°C.
- Two high pressure piston pumps (single or double piston) and appropriate filters, stainless steel tubing and fittings to pump aqueous solutions from reservoirs into autoclave at working pressure.
- Gravity or vacuum filtration equipment for washing product.

Reagents*Si solution*

Appropriate concentration of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) in distilled/deionised water.

Si + NaOH solution

Appropriate concentrations of sodium metasilicate plus sodium hydroxide (NaOH) in water

Ca solution

Appropriate concentration of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in water.

Example 6**Method for making Pectolite in a 2ℓ autoclave (of Monel 400 alloy)***Si + NaOH solution*

Dissolve together 0.040 mole (8.48g) of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ plus 0.20 mole (8.0g) of NaOH made up to 600g with water and transfer to reservoir of pump No. 1.

Ca solution

Dissolve 0.020 mole (4.72g) of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in water and make up to 600g. Transfer to reservoir of pump No. 2.

Place sufficient water in the autoclave to fill it with steam at the working temperature, and still have approximately 50ml liquid, e.g. at 274°C, ρ steam = 30.26 g/l and ρ water = 760 g/l therefore require $30.26 \times 1.95 + 760 \times 0.05 = 59 + 38 = 97\text{g}$

Seal the autoclave and heat to an interior temperature of $\geq 250^\circ\text{C}$.

After priming both the pumps, begin pumping the (Si + NaOH) solution (Pump No. 1) into the autoclave at a suitable rate (e.g. 150ml/hr). After a few mls have been pumped, begin pumping the Ca solution at the same rate. Low speed stirring may improve the product. When the reservoirs are nearly empty, turn off the pumps and shortly afterwards (so that sufficient reaction time above 250°C, is allowed to use up the reagent), turn off the autoclave heater.

When cool, remove the product by suitable means, e.g. siphoning (if a bottom flush valve is used, the fibres can prevent resealing. If a very concentrated product is made, siphoning is far more satisfactory).

Wash the product with water by a suitable means, e.g. dilute and decant, filter and wash.

Product can be analysed by XRD and SEM. The product of this run was near-acicular (needle-like) fibres having minimal branching, length approx 11 to 62 μm ; thickness approx 0.1 to 1.0 μm . Average length approx 30 μm .

Process tolerance

Concentrations

In a 2 litre autoclave, we have made between 0.16g and 100g of product by the pure (i.e. premixed) batch method. When the solutions are pumped, the process can tend to form large lumps of product (up to tens of grams) if the solution concentrations are above approximately 0.1-0.2 molar.

Reagent ratios

The Ca:Si ratio is preferably varied between approximately 0.25 and 0.65 without forming other phases. The stoichiometric Ca:Si of Pectolite ratio is 0.67, but the process appears to produce better product morphology if excess Si is present, i.e. use Ca:Si of <0.67.

The NaOH concentration can vary widely, but if it is too low, fibre size tends to be small; if too high, rapid discoloration (corrosion) of the vessel will occur. Preferred NaOH concentration range is approximately 0.05M-1.0M.

Temperature

Higher temperature decreases formation time and tends to increase fibre size. High pH combined with high temperature will maximise formation rate and fibre quality.

pH \geq 13.5-14.

Temperature vs time for formation of Pectolite

At 350°C, Pectolite can be fully formed in approximately 30-60 minutes.

At ~290°C, is less than or equal to 4 hours.

At 212°C, 18 hours.

At 196°C, approximately 94 hours.

Example 7**Production of fibres using one pump only (semi-batch process)**

If using only one pump, the Si and NaOH solution must be placed in the autoclave before heating commences. The Ca salt solution can be pumped into the vessel once the necessary internal temperature is reached. Compared with the pure batch process, there is no clear indication that average fibre size is increased or decreased, however a wider range of fibre size is produced (i.e. standard deviation of fibre size).

NB: (1) NaOH cannot be pumped with the calcium nitrate as insoluble $\text{Ca}(\text{OH})_2$ will immediately precipitate; (2) When Ca and NaOH were placed in vessel and Si pumped, the result was a thin non-fibrous layer comprising ite, Tobermorite, calcite and amorphous material.

Example 8

The following four preparations were directed to the preparation of fibrous product containing Pectolite and Xonotlite. In each case the preparation involved the use of pumps with preparation (a) following the general procedure of Example 7 (ie a one pump process) and preparations (b), (c) and (d) following the general procedure as used in Example 6 (ie a two pump process).

(a) Solution A contained 11.81 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in distilled water to a total of 1000 grams. Solution B contained 21.21 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 20 grams NaOH, dissolved in water to total 500 grams. Solution A was pumped over a period of 2.5 hours into a 2 litre autoclave, pre-heated to 247°C which, before heating, had been charged

with Solution B. After the pumping of Solution A was finished, the autoclave was held at 247°C temperature for 0.5 hours then turned off to cool down over several hours. The product was discrete fibres of pure Pectolite as is shown in Figure 6.

(b) Solution A contained 11.34 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in distilled water to total 700 grams. Solution B contained 10.18 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 8 grams NaOH, dissolved in water to total 700 grams. Solution C contained 100 grams water. Solutions A and B were pumped simultaneously over a period of 4.6 hours into a 2 litre autoclave, preheated to 270°C which, before heating, was charged with solution C. After the pumping of solutions A and B had finished the autoclave was turned off and allowed to cool down over several hours. The product produced was discrete fibres composed mostly of Xonotlite as is shown in Figure 7.

(c) Solution A contained 5.15 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in distilled water to total 500 grams. Solution B contained 9.25 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, dissolved in water to total 500 grams. Solution C contained 25 grams of NaOH dissolved in water to total 200 grams. Solutions A and B were pumped simultaneously over a period of 7.5 hours into a 2 litre autoclave, preheated to 260°C which, before heating, was charged with solution C. After the pumping of solutions A and B had finished the autoclave was held at 267°C for two hours and then turned off and allowed to cool down over several hours. The product was discrete fibres of pure Pectolite as is shown in Figure 8.

(d) Solution A contained 31.49 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in distilled water to total 200 grams. Solution B contained 42.42 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, dissolved in water to total 400 grams. Solution C contained 42.42 grams of $\text{NaSiO}_3 \cdot 5\text{H}_2\text{O}$ and 16 grams of NaOH and 15.74 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in water to total 500 grams. Solutions A and B were pumped simultaneously over a period of 2.4 hours into a 2 litre autoclave, preheated to 300°C which, before heating, was charged with solution C. After the pumping of solutions

A and B had finished the autoclave was held at 302°C for 1.6 hours and then turned off and allowed to cool down over several hours. The product was discrete fibres of pure Pectolite as is shown in Figure 9.

As can be seen in all instances (Figures 6 to 9) the fibres produced are discrete fibres of a relatively standard length. Such standard fibre length allows the use of such fibres in specific reinforcement requirements.

Examples 9 to 20

The following Examples were run using the pure batch method as disclosed generally in connection with Example 1.

Example 9

A pure batch reaction was carried out by dissolving 0.2727 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0.800 grams of NaOH in 10 ml of distilled water and 0.4049 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 5 ml of distilled water and adding this to the first solution. The resulting gel was made up to 20.0 grams in an 80 ml pressure vessel which was sealed and heated at autogenous pressure at 349°C for six hours in a tube furnace. The vessel was air cooled after the run. The product was mostly discrete fibres of Foshagite as is shown in the Figure 10. The average length of the fibres is 23 μm with a percentage standard deviation of 31%.

Example 10

A pure batch reaction was carried out by dissolving 0.3182 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0.800 grams of NaOH in 10 ml of distilled water and 0.3543 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 5 ml of distilled water and adding this to the first solution. The resulting gel was made up to 20.0

grams in an 80 ml pressure vessel which was sealed and heated at autogenous pressure at 365°C for 6.25 hours in a tube furnace. The vessel was air cooled after the run. The product was mostly discrete fibres of Foshagite as is shown in the Figure 11. The average length of the fibres is 24 μm and the percentage standard deviation is 37%.

Example 11

A pure batch reaction was carried out by dissolving 0.2121 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0.8 grams of NaOH in 10 ml of distilled water and 0.4724 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 5 ml of distilled water and adding this to the first solution. The resulting gel was made up to 20.0 grams in a 25 ml pressure vessel which was sealed and heated at autogenous pressure at 240°C for 16 hours in a fan oven. The vessel was cooled with its lower half in cold water after the reaction. The product was mostly discrete fibres of Hillebrandite as is shown in Figure 12. The average length of the fibres is 30 μm and the percentage standard deviation is 31%.

Example 12

A pure batch reaction was carried out by dissolving 0.2728 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0.800 grams of NaOH in 10 ml of distilled water and 0.4053 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 5 ml of distilled water and adding this to the first solution. The resulting gel was made up to 20.0 grams in a 25 ml pressure vessel which was sealed and heated at autogenous pressure at 240°C for 16 hours in a fan oven. The vessel was cooled with its lower half in cold water after the reaction. The product was discrete fibres of pure Foshagite as is shown in Figure 13. The average length of the fibres is 26 μm and the percentage standard deviation is 25%.

Example 13

A pure batch reaction was carried out by dissolving 0.452 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0.160 grams of NaOH in 10 ml of distilled water and 0.252 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 5 ml of distilled water and adding this to the first solution. The resulting gel was made up to 20.0 grams in a 25 ml pressure vessel which was sealed and heated at autogenous pressure at 300°C for 16 hours in a fan oven. The vessel was cooled with its lower half in cold water after the reaction. The product was discrete fibres of pure Pectolite as is shown in Figure 14. The average length of the fibres is 95 μm and the percentage standard deviation is 47%.

Example 14

A pure batch reaction was carried out by dissolving 0.452 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0 grams of NaOH in 10 ml of distilled water and 0.252 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 5 ml of distilled water and adding this to the first solution. The resulting gel was made up to 20.0 grams in a 25 ml pressure vessel which was sealed and heated at autogenous pressure at 300°C for 16 hours in a fan oven. The vessel was cooled with its lower half in cold water after the reaction. The product was discrete fibres of pure Pectolite as is shown in Figure 15. The average length of the fibres is 15 μm and the percentage standard deviation is 36%.

Example 15

A pure batch reaction was carried out by dissolving 4.242 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 8 grams of NaOH in 750 ml of distilled water and 2.362 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 350 ml of distilled water and adding this to the first solution. The resulting gel was made up to 1250 grams in a 2000 ml pressure vessel which was sealed and heated at autogenous pressure at 315°C for 10 hours. The vessel was cooled in air after the run. The product was discrete fibres of pure Pectolite as shown in Figure 16. The average length of the fibres is 80 μm and the percentage standard deviation is 45%.

Example 16

A pure batch reaction was carried out by dissolving 113.7 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 9.25 grams of NaOH in 750 ml of distilled water and 168.7 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 350 ml of distilled water and adding this to the first solution. The resulting gel was made up to 1250 grams in a 2000 ml pressure vessel which was sealed and heated at autogenous pressure at 325°C for 18 hours. The vessel was cooled quickly after the run with a water cooled coil. The product was mostly discrete fibres of Foshagite as shown in Figure 17. The average length of the fibres is 11 μm and the percentage standard deviation is 34%.

Example 17

A pure batch reaction was carried out by dissolving 0.3182 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0.8 grams of NaOH in 10 ml of distilled water and 0.3543 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 5 ml of distilled water and adding this to the first solution. The resulting gel was made up to 20 grams in a 25 ml pressure vessel which was sealed and heated at autogenous pressure at 240°C for 16 hours in a fan oven. The vessel was cooled with its lower half in cold water after the run. The product was mostly discrete fibres of Foshagite as shown in Figure 18. The average length of the fibres is 22 μm and the percentage standard deviation is 34%.

Example 18

A pure batch reaction was carried out by dissolving 21.21 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 10 grams of NaOH in 600 ml of distilled water and 11.81 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 200 ml of distilled water and adding this to the first solution. The resulting gel was made up to 1000 grams in a 2000 ml pressure vessel which was sealed and heated at autogenous pressure at 207°C for 6 hours. The vessel was air cooled after the run. The product was discrete fibres of pure Tobermorite as shown in Figure 19. The approximate average length of the fibres is

2 μm and the approximate percentage standard deviation is 50%. The approximate nature of the figures is due to the extremely small fibre length.

Example 19

A pure batch reaction was carried out by dissolving 27.92 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 3.07 grams of NaOH in 700 ml of distilled water and 27.96 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 400 ml of distilled water and adding this to the first solution. The resulting gel was made up to 1250 ml in a 2 l pressure vessel which was sealed and heated at autogenous pressure at 320°C for 4 hours. The vessel was air cooled after the run. The product was discrete fibres of pure Xonotlite as shown in Figure 20. The average length of the fibres is 4 μm and the percentage standard deviation is 44%.

Example 20

A pure batch reaction was carried out by dissolving 55.81 grams of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 3.95 grams of NaOH in 700 ml of distilled water and 55.95 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 400 ml of distilled water and adding this to the first solution. The resulting gel was made up to 1250 ml in a 2 l pressure vessel which was sealed and heated at autogenous pressure at 320°C for 4 hours. The vessel was air cooled after the run. The product was discrete fibres of pure Xonotlite as shown in Figure 21. The average length of the fibres is 5 μm and the percentage standard deviation is 33%.

Example 21

The following three preparations as shown in Table 1 were prepared by the pure batch method and were directed to the production of a fibrous product containing a majority of Pectolite.

The Pectolite content is approximately 60% or above. These preparations show the differences in fibre length on an average basis which can be obtained by varying the starting ratio of Ca:Si and the temperature. The greatest separation of length is +/- 15 μm which is within commercially acceptable levels.

Table 1

Run	Ca:Si	Temperature $^{\circ}\text{C}$	Fibre Length (μm)	Figure
1	0.76	324	30-50	19
2	0.333	312	20-30	20
3	0.733	290	20-50	21

Example 22

The following preparations shown in Table 2 were carried out as for Example 19. The preparations were intended to produce a fibrous material containing a major amount of Foshagite (approximately 60% or more). Again the combination of the Ca:Si ratio and temperature gives standard fibre lengths in discrete form with the greatest separation in fibre length being +/- 10 μm .

Table 2

Run	Ca:Si	Temperature $^{\circ}\text{C}$	Fibre Length (μm)	Figure
1	0.90	260	20	22
2	1	365	20-30	23
3	1.60	260	20-25	24

Comparisons

Use of two pumps results in the fibres being larger than for the pure batch or single pump method, because fresh reagent is continually added to allow growth of existing fibres. New fibres, however, will be continually formed and later ones will therefore tend to be smaller.

Therefore, there is a wide range of fibre size. There appears to be no clear advantage in using the single pump method over the pure batch method because average fibre size is similar, and the fibre size range is greater.

(NB: The pure batch method (unpumped) is equivalent to a continuous flow production plant fed only by a single inlet, so that the product would depend on the initial ratios, residence time and temperature. The 2-pump system is equivalent to the above-described plant, but with continual addition of nutrient to enlarge existing fibres and form new, small fibres).

Tables 3-5 give example ranges of conditions at which crystal phases have been formed in this project (in Near-pure form and in Impure (mixed phases) form). With reference to Table 5, the pH of the mixture is controlled by the concentration of alkali present as will be known in the art. Table 5 gives this as the Na₂O concentration. The Na is sourced from the soluble sodium salt used and/or the added NaOH. The example ranges should not be seen to be limitations on the process conditions however.

Table 3
Calcium:Silicate ratio (Ca:Si)

	NEAR-PURE	IMPURE
Pectolite	0.76 (208) 0.20 (267)	1.33 (166) 0.20 (267)
Tobermorite	0.50 (241) 0.50 (178)	2.00 (274) 0.33 (52)
Xonotlite	5.00 (275) 1.00 (47)	5.00 (268) 0.50 (245)
Foshagite	1.33 (243) 1.00 (182)	2.00 (46) 0.833 (169)
Hillebrandite	2.00 (146) 2.00 (181)	2.00 (122) 2.00 (256)

Numbers in brackets are prep numbers (for reference)

Table 4
Temperature °C

	NEAR-PURE	IMPURE (mixed)

Pectolite	361°C (168) 198°C (279)	365°C (167) 198°C (279)
Tobermorite	305 (241, KOH only) 160 (277)	255 (69) 305 (241, KOH only) 172 (13)
Xonotlite	268 (252) 247 (47)	340 (209) 172 (13)
Foshagite	313 (243) 240 (147)	365 (167) 235 (132)
Hillebrandite	284 (181) 240 (146)	364 (165) 235 (131)

TABLE 5
ALKALI CONCENTRATION IN SOLUTION AS Na_2O
(moles/kg of prep)

	NEAR-PURE	IMPURE
Pectolite	0.800 (219) 0.100 (257)	1.08 (164) 0.050 (269)
Tobermorite	0.225 (178) 0 (241) ($\text{K}_2\text{O}=0.20\text{M}$)	0.59 (151) 0.013 (130)
Xonotlite	0.125 (252) 0.033 (268)	0.58 (148) 0.033 (268)
Foshagite	0.565 (147) 0.107 (243)	1.033 (189) 0 (182) ($\text{K}_2\text{O}-0.60\text{M}$)
Hillebrandite	0.55 (146) 0.050 (181) ($\text{K}_2\text{O}=0.50$)	0.55 (146) 0.050 (181) ($\text{K}_2\text{O}-0.50$)

The foregoing describes preferred forms of the invention and it is to be understood that the scope of the invention is not to be limited to the specific forms described. Modifications and variations as will be obvious to a person skilled in the art may be made to the forms of the invention as described without departing from the spirit or scope of the invention as defined in the attached claims.

CLAIMS:

1. A method for the production of discrete fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates of predetermined average fibre length comprising mixing an aqueous solution of a soluble calcium salt with a soluble silica source and heating the mixture to form the fibrous product.
2. The method according to claim 1 comprising the steps of:
 - (a) preparing an aqueous gel solution of a soluble calcium salt and a soluble silica source having a specific molar ratio of calcium:silica effective to produce predetermined fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates;
 - (b) heating the aqueous gel solution to a temperature and for a time effective to produce the predetermined fibrous hydrates at said predetermined length; and
 - (c) recovering the product.
3. The method according to claim 1 or claim 2 wherein the temperature to which the aqueous solution is heated is between about 140°C and 400°C.
4. The method according to claim 3 wherein the temperature is between 170°C and 360°C.
5. The method according to claim 4 wherein the temperature is between 250°C and 300°C.
6. The method according to any one of the previous claims wherein the calcium:silica molar ratio is between 0.2 and 5.0.

7. The method according to claim 6 wherein the molar ratio is between 0.5 and 2.5.
8. The method according to any one of the previous claims wherein the mixture is heated for between about 1 and about 6 hours.
9. The method according to claim 8 wherein the mixture is heated for between 2 and 5 hours.
10. The method according to claim 1 wherein the method is for the preparation of discrete calcium silicate fibres including the sodium calcium silicate hydrate Pectolite comprising mixing a soluble calcium salt with a soluble silica source and a soluble sodium salt in a Ca:Si ratio of from about 0.20 to about 0.76 and heating the mixture to a temperature of between about 200°C and 365°C to obtain discrete fibres having a length of between about 25 and about 60 μm .
11. The method according to claim 1 wherein the method is for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate Tobermorite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 0.45 to about 2.0 and heating the mixture to a temperature of between about 150°C and about 305°C, to obtain discrete fibres having a length of between 1 and about 15 μm .
12. The method according to claim 1 wherein the method is for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate Xonotlite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 0.8 to about

5.0 and heating the mixture to a temperature of between 250°C and 320°C, to obtain discrete fibres having a length of between about 2 and about 15 μm .

13. The method according to claim 1 wherein the method is for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate Foshagite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 0.80 to about 1.60 and heating the mixture to a temperature of between 235°C and about 315°C, to obtain discrete fibres having the length of between about 15 and about 40 μm .

14. The method according to claim 1 wherein the method is for the preparation of discrete calcium silicate fibres including the calcium silicate hydrate hillebrandite comprising mixing a soluble calcium salt with a soluble silica source in a Ca:Si ratio of from about 1.67 to 2.50 and heating the mixture to a temperature of between 235°C and about 370°C, to obtain discrete fibres having a length of between about 10 and about 55 μm .

15. The method according to any one of the previous claims wherein the product comprises a mixture of fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates.

16. The method according to any one of the previous claims wherein the length of the fibres produced is between about 1 μm and about 500 μm .

17. The method according to claim 16 wherein the fibre length is between about 2 and about 300 μm .

18. The method according to claim 17 wherein the fibre length is between about 2 and about 200 μm .
19. The method according to any one of the previous claims wherein the fibre lengths have a percentage standard deviation of less than about 45%.
20. The method according to claim 19 wherein the standard deviation is less than 35%.
21. The method according to any one of the previous claims wherein the soluble calcium salt is calcium nitrate or calcium chloride.
22. The method according to any one of the previous claims wherein the soluble silica source is an alkaline silicate.
23. The method according to claim 22 wherein the alkaline silicate is sodium silicate.
24. The method according to claim 10 wherein the soluble silica source and the soluble sodium salt both comprise sodium silicate.
25. The method according to either claim 10 or claim 24 wherein the soluble sodium salt includes additional NaOH.
26. The method according to any one of the previous claims wherein the calcium salt solution is premixed with the soluble silica source and then heated.

27. The method according to any one of the previous claims wherein the soluble silica source is an aqueous solution.

28. The method according to any one of claims 1 to 25 wherein the soluble silica solution is preheated in a sealed vessel and the soluble calcium salt solution is pumped into the vessel.

29. The method according to any one of the previous claims wherein an additional potassium hydroxide is added to the silicate solution.

30. The method of any one of claims 1 to 25 wherein the soluble silica solution and the soluble calcium salt are pumped separately into a preheated seal vessel.

31. The method according to any one of the previous claims wherein the solutions are heated in a sealed vessel.

32. The method according to claim 31 wherein the sealed vessel is an autoclave.

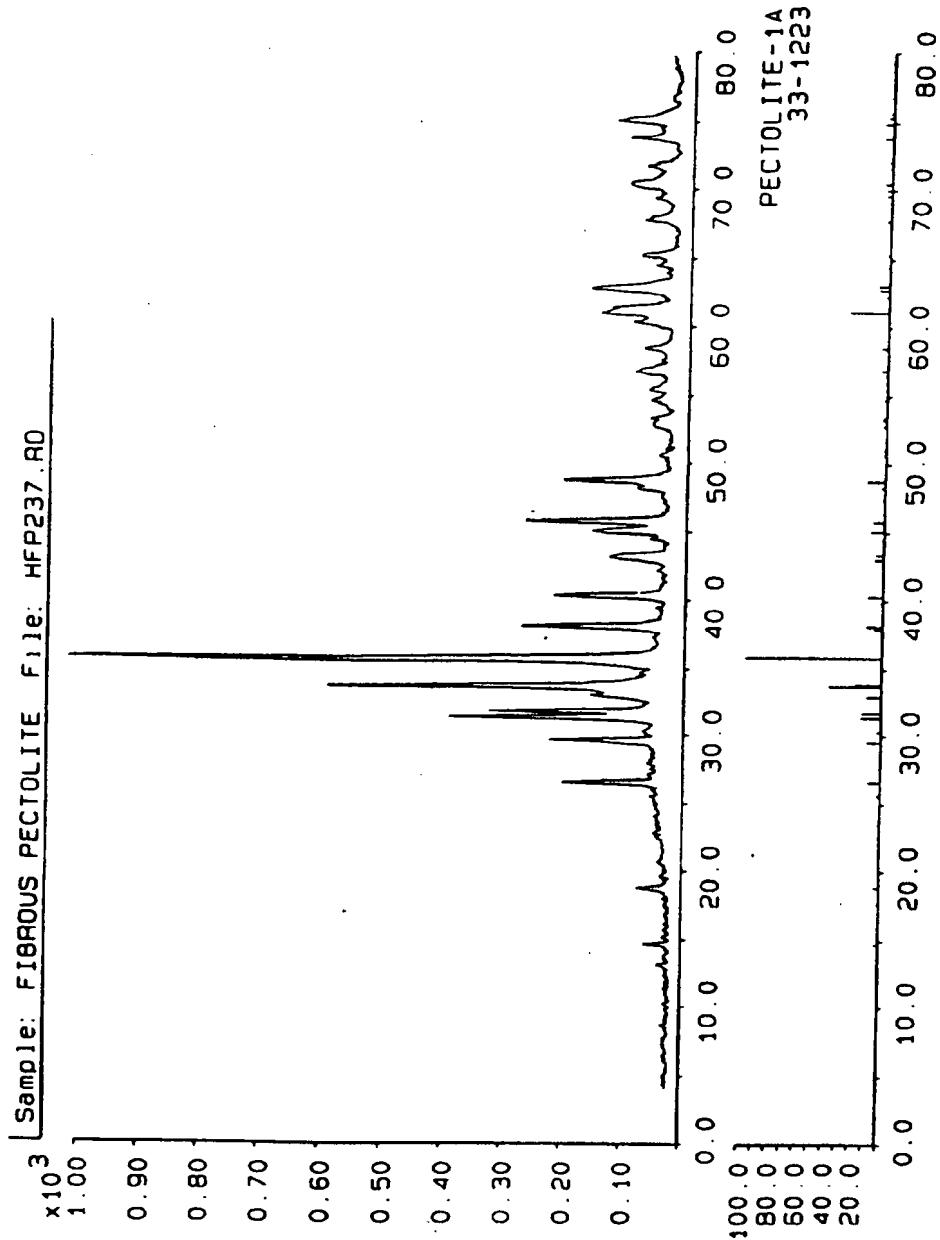
33. A fibrous product comprising discrete fibrous calcium silicate hydrates and/or calcium sodium silicate hydrates prepared by the method of any one of the previous claims.

34. A method for the production of discrete fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates substantially as herein described with particular reference to the Examples and attached Figures.

ABSTRACT

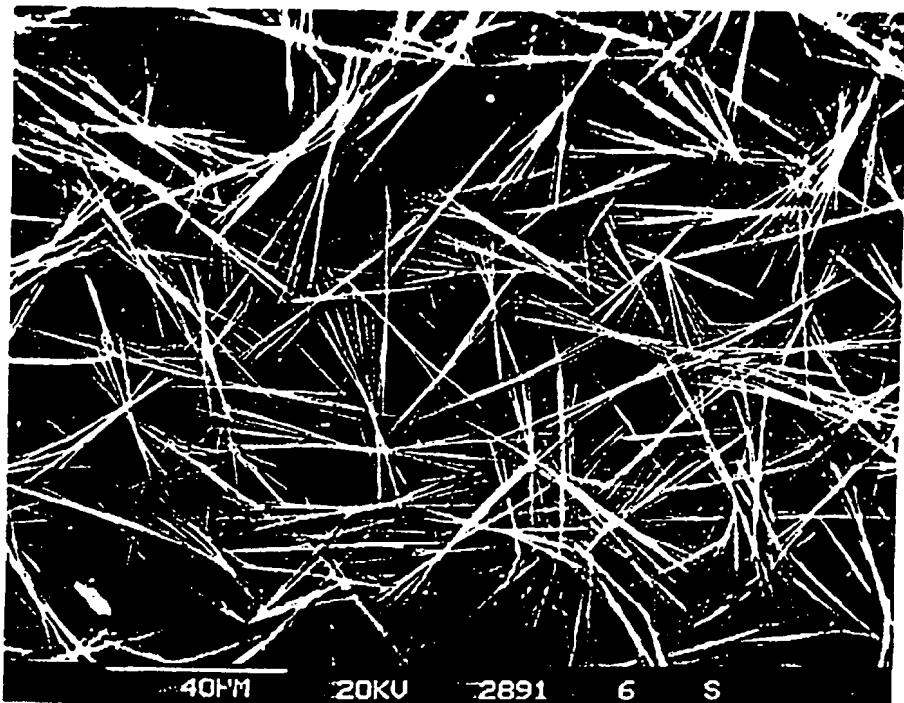
A method for the production of discrete fibrous calcium silicate hydrates and/or sodium calcium silicate hydrates of predetermined average fibre length comprising mixing an aqueous solution of a soluble calcium salt with a soluble silica source and heating the mixture to form the fibrous product.

FIG 1A



1/21

FIG 1B



2/21

FIG 1C

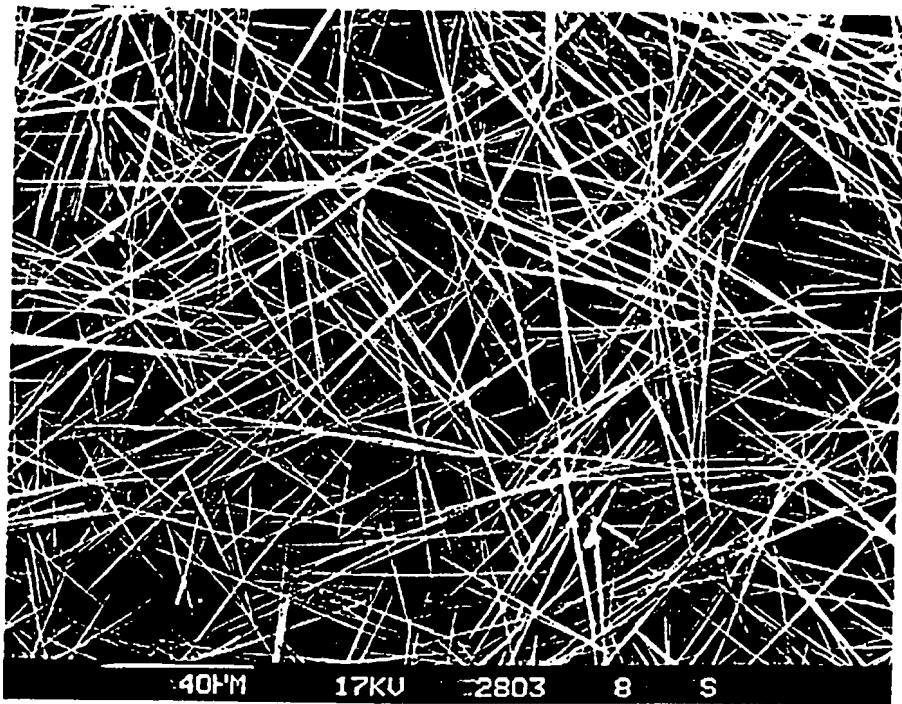


FIG 1D

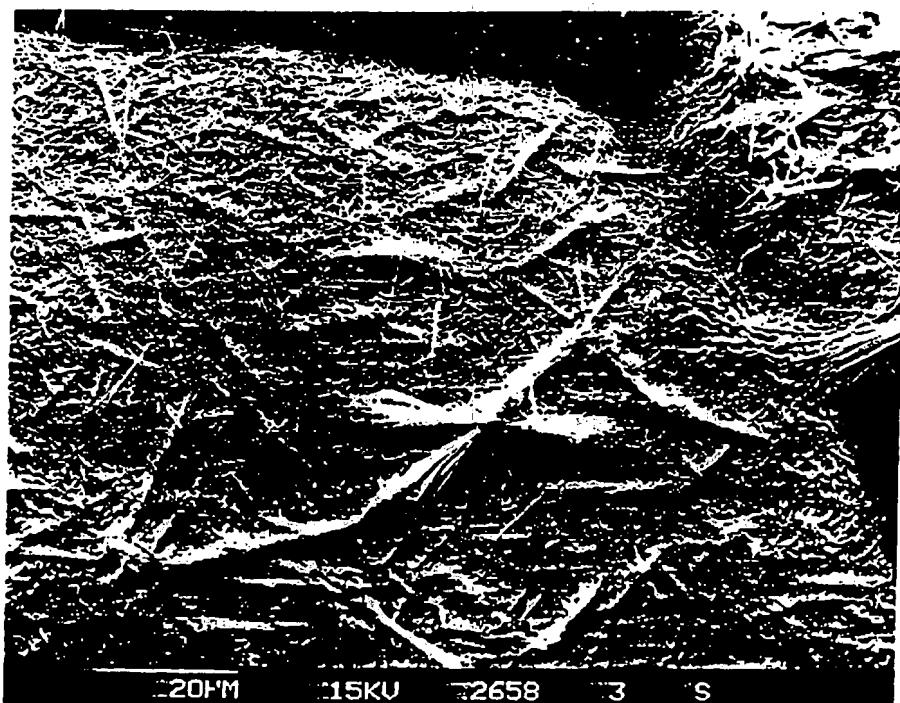


FIG 2A

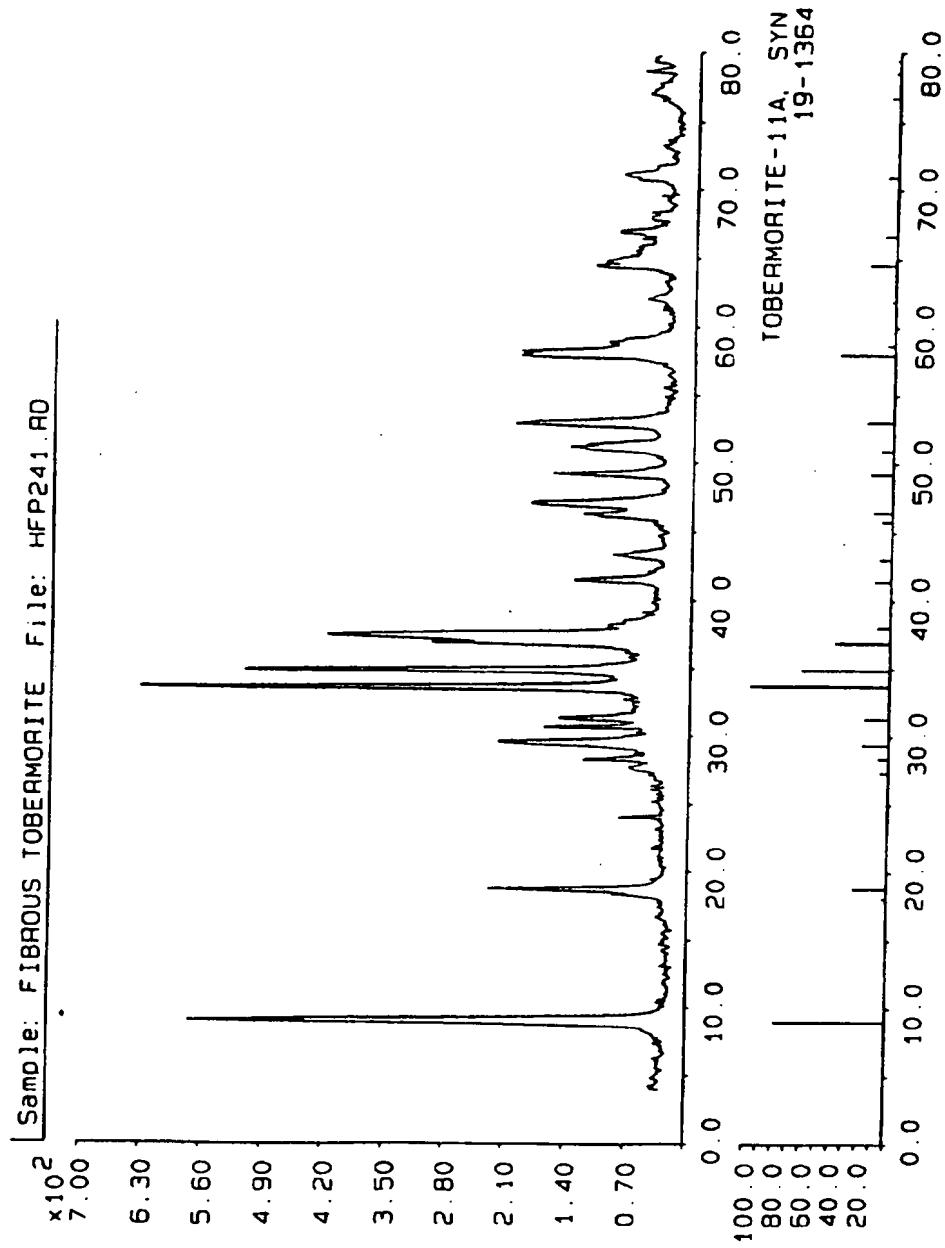
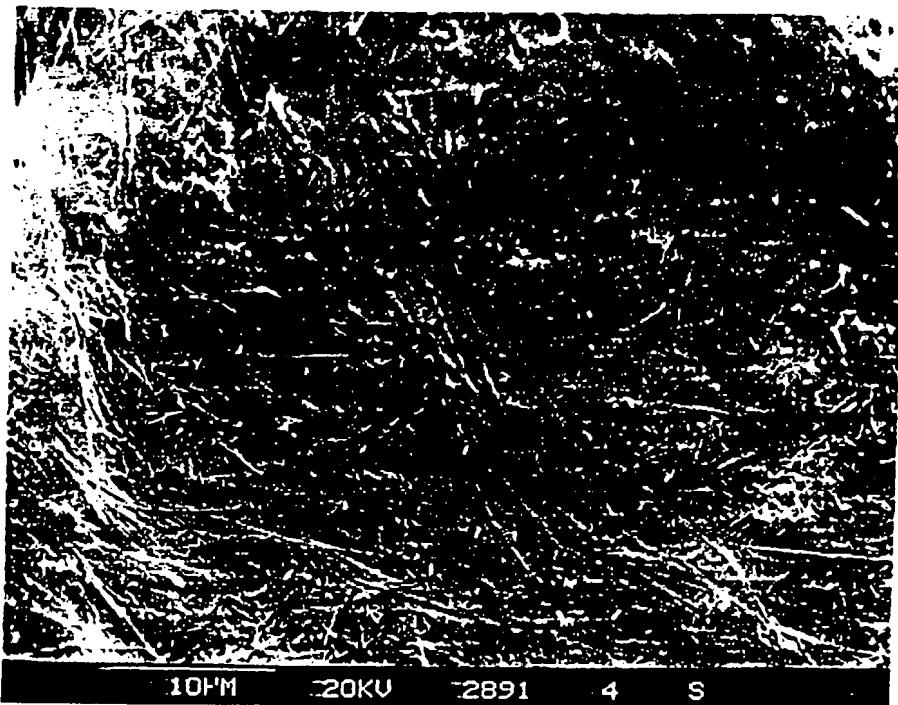


FIG 2B



6/21

SUBSTITUTE SHEET

FIG 3A

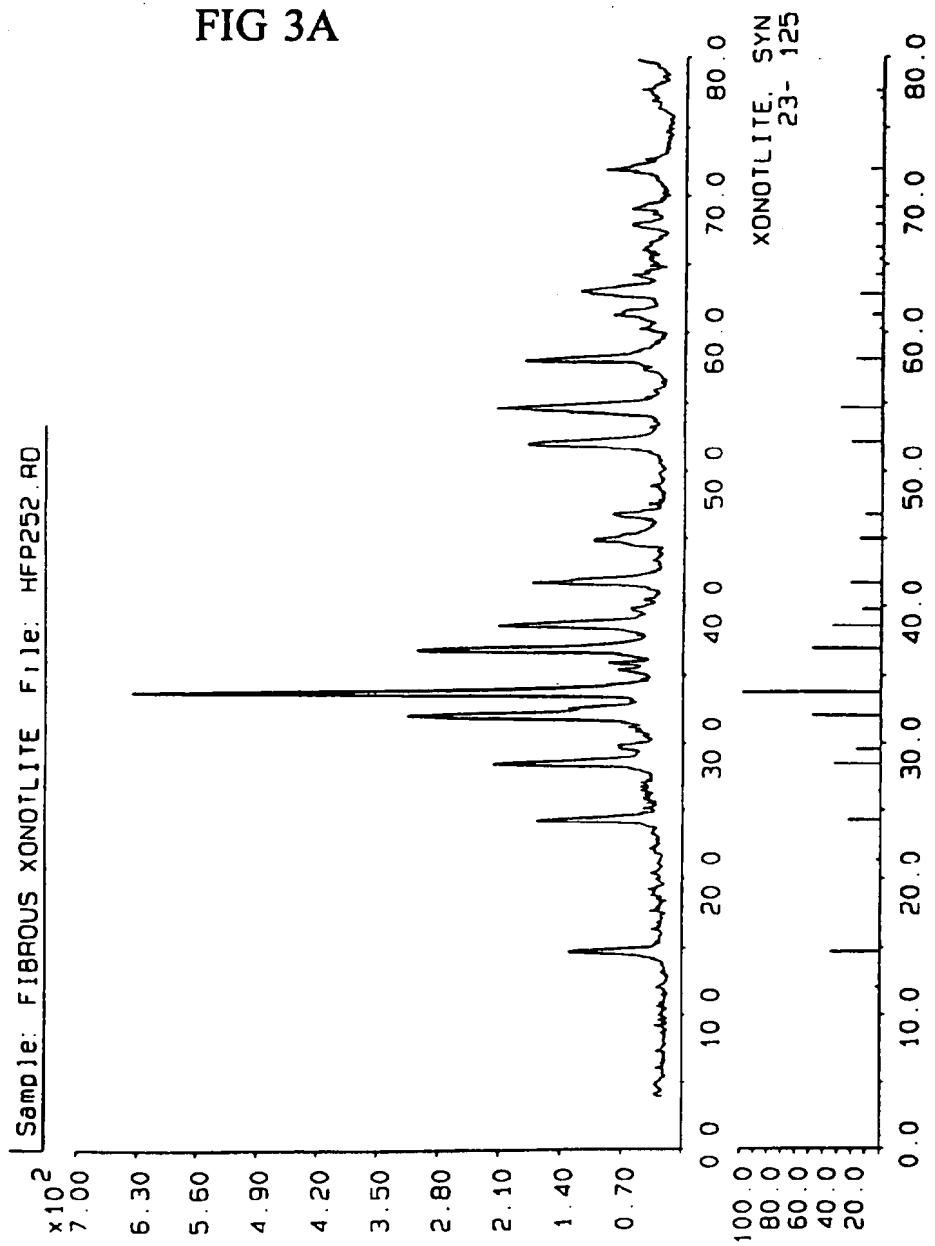


FIG 3B

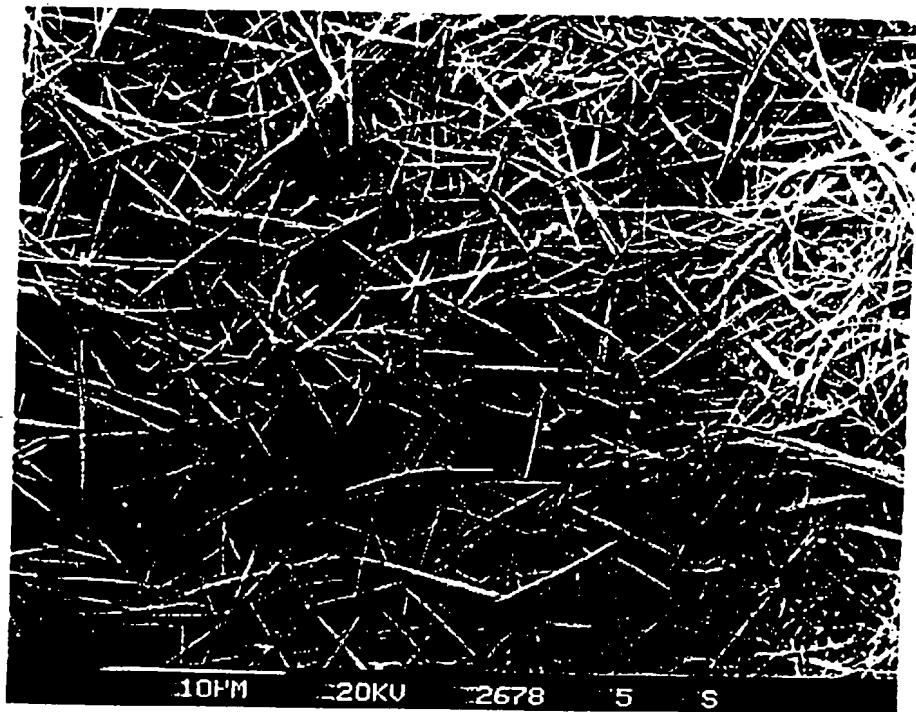


FIG 4A

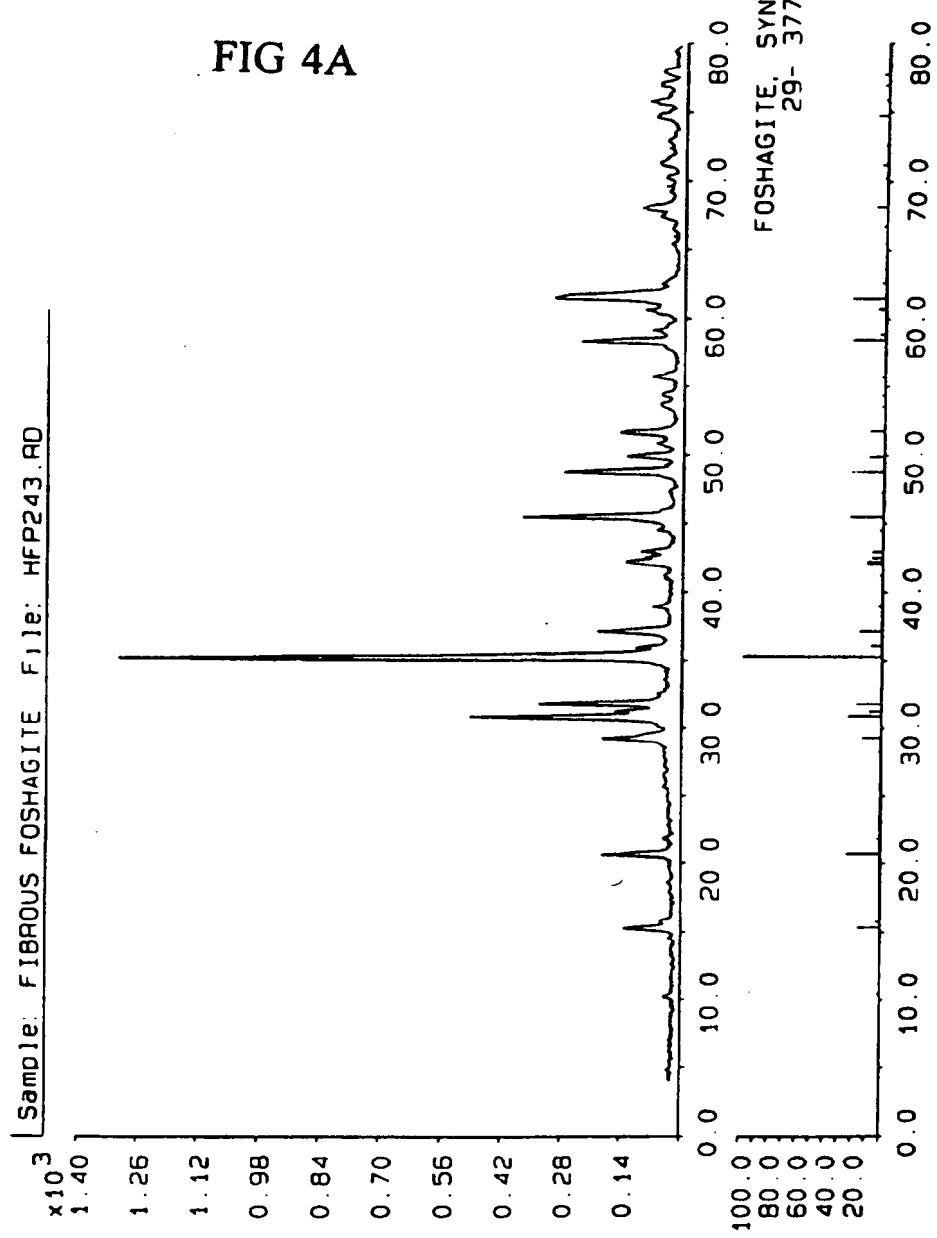
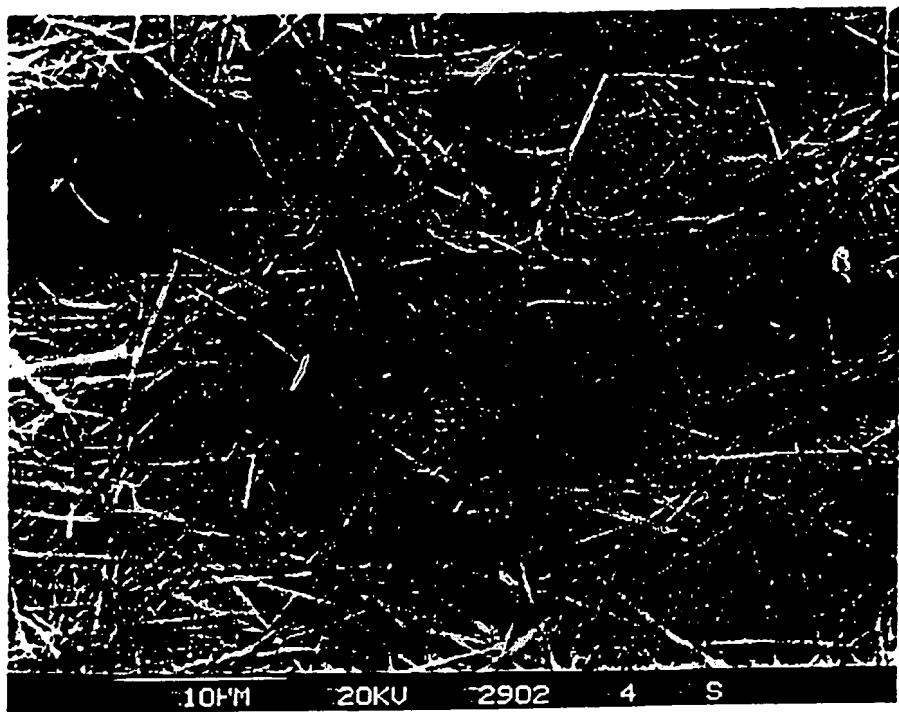


FIG 4B



10/21

SUBSTITUTE SHEET

FIG 5A

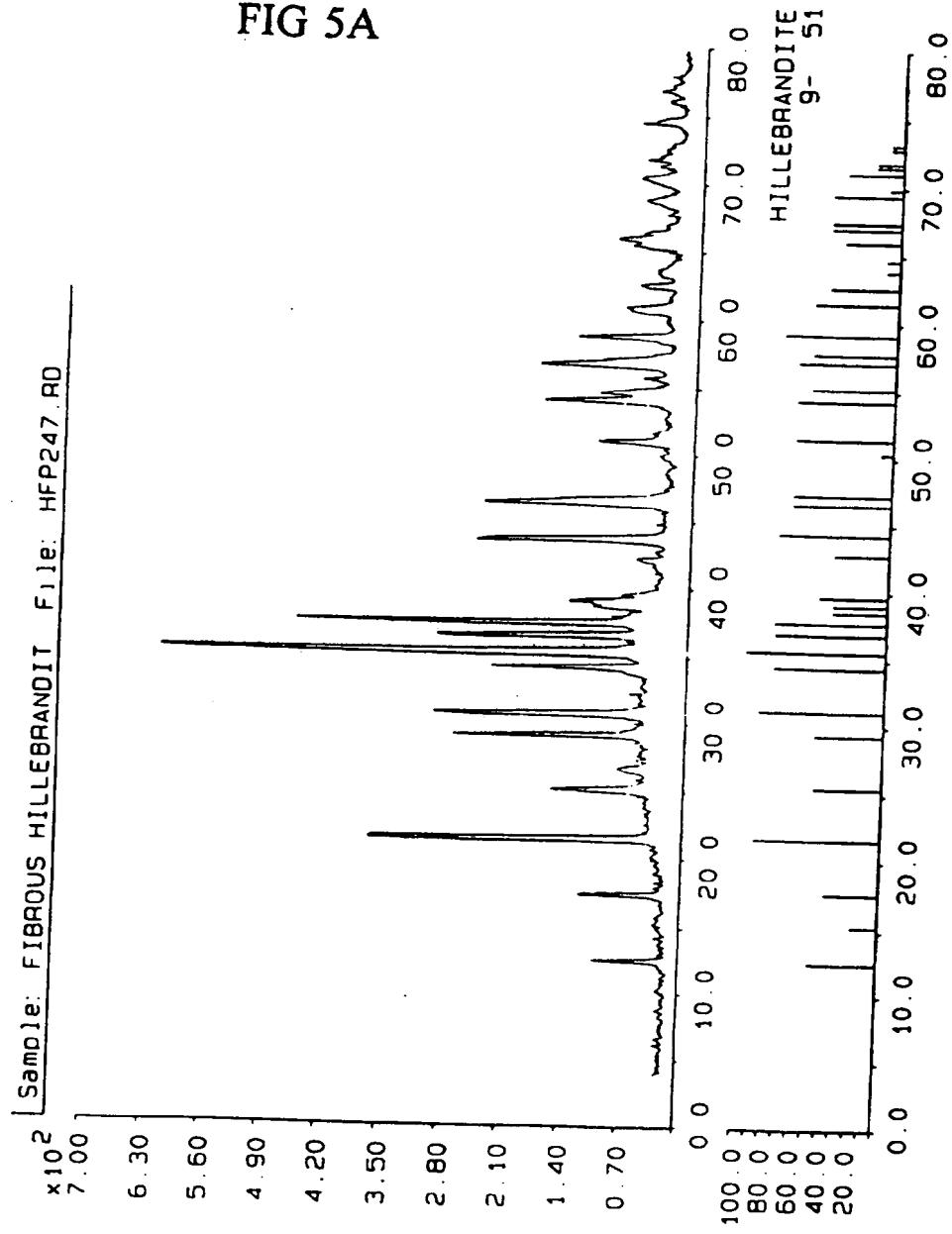


FIG 5B

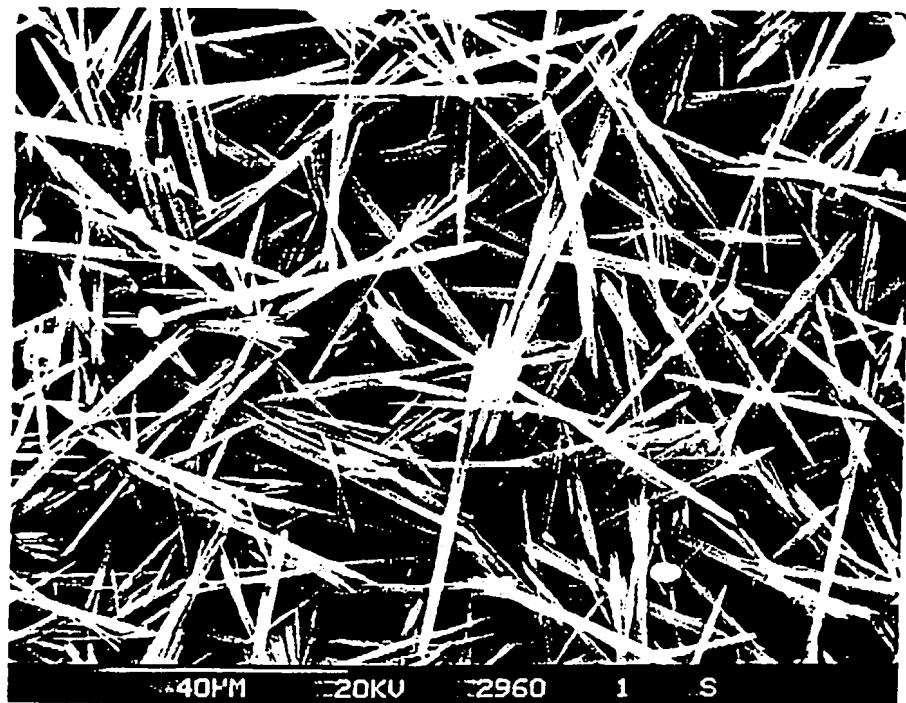


FIG 6

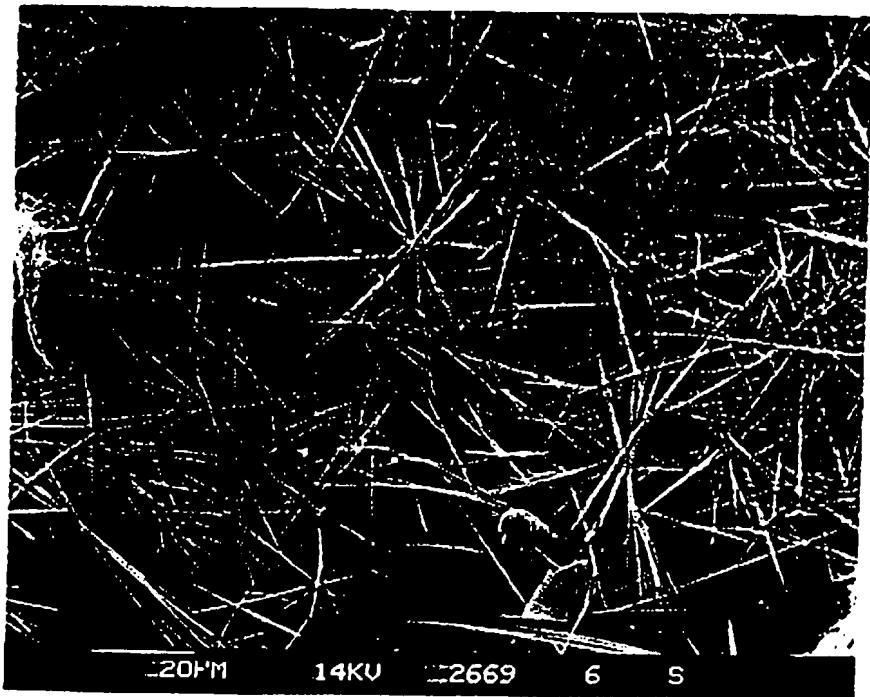


FIG 7

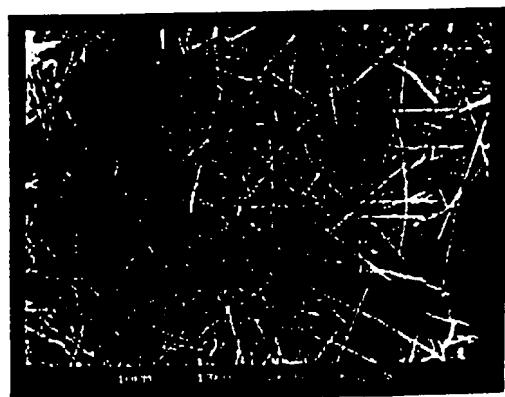


FIG 8

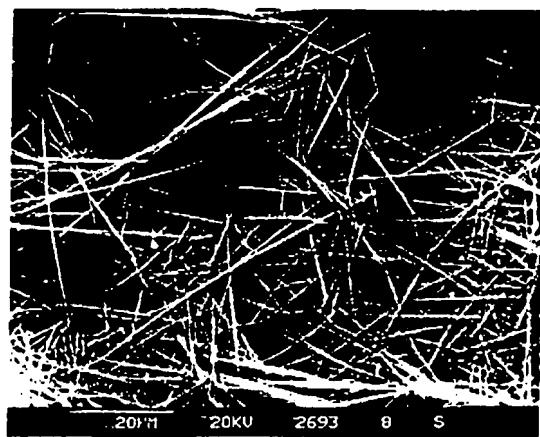


FIG 9

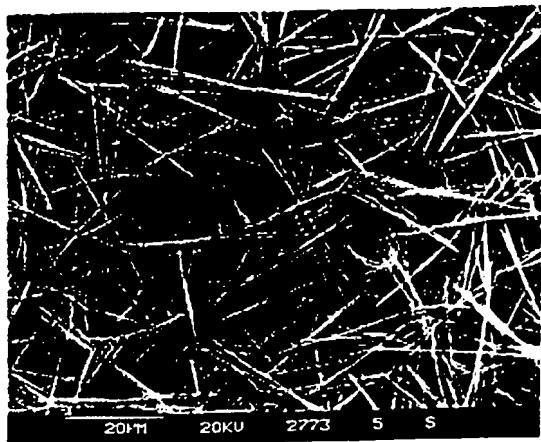


FIG 10

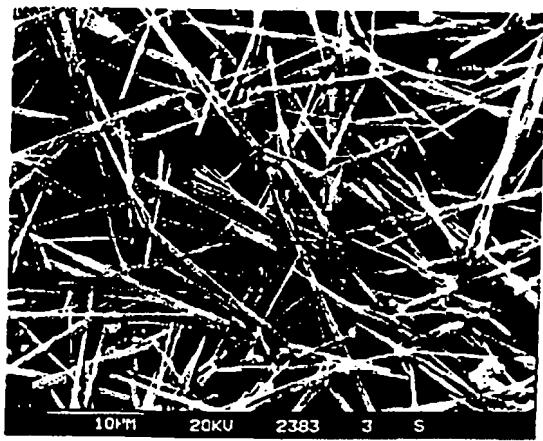


FIG 11

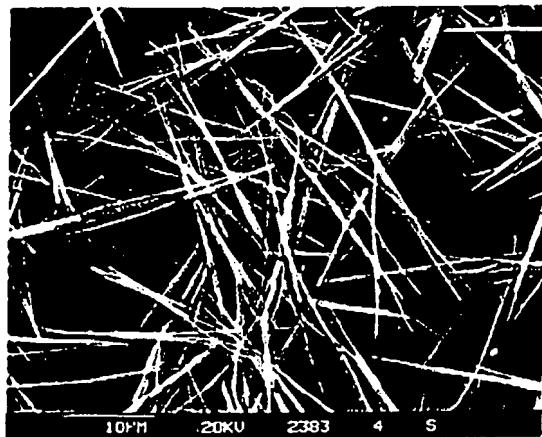


FIG 12

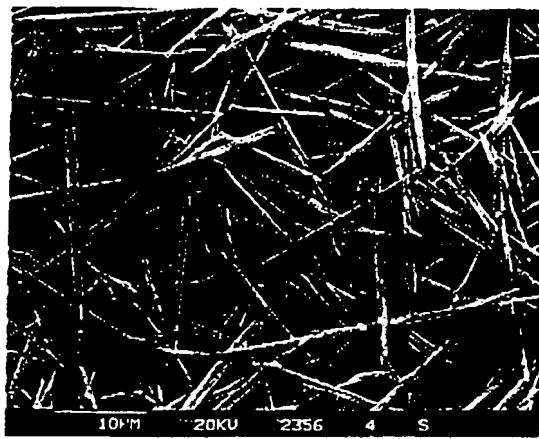


FIG 13

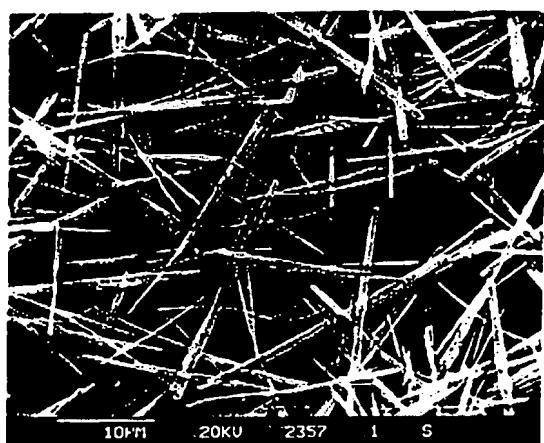


FIG 14

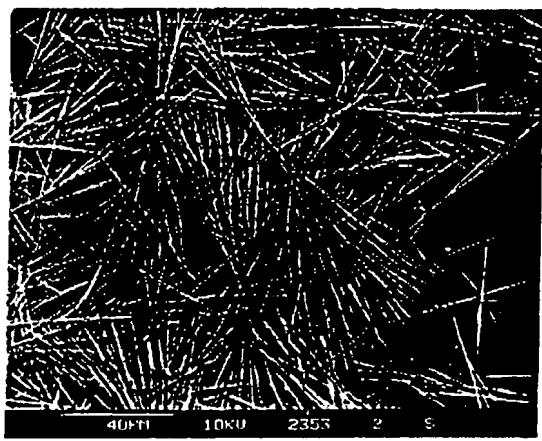


FIG 15

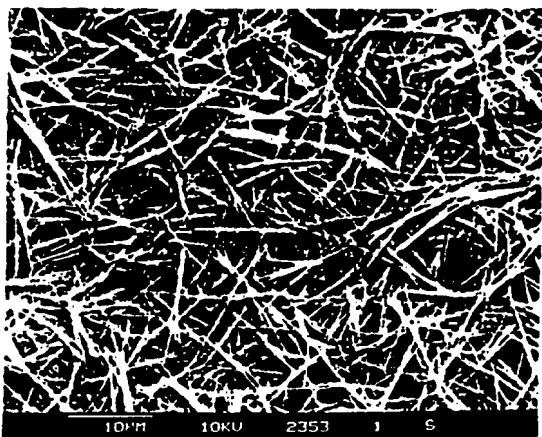


FIG 16

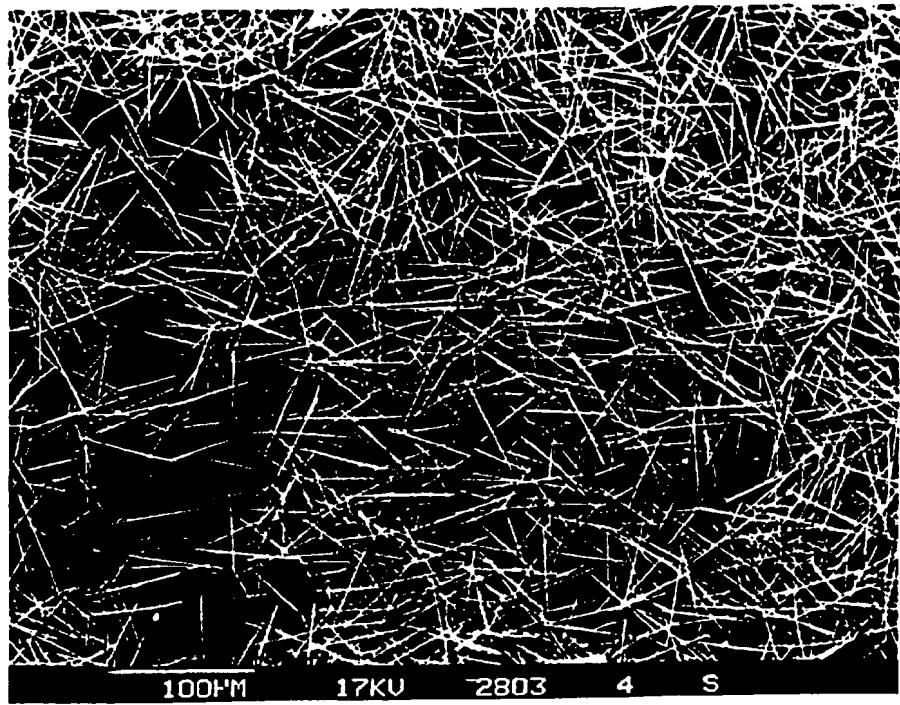
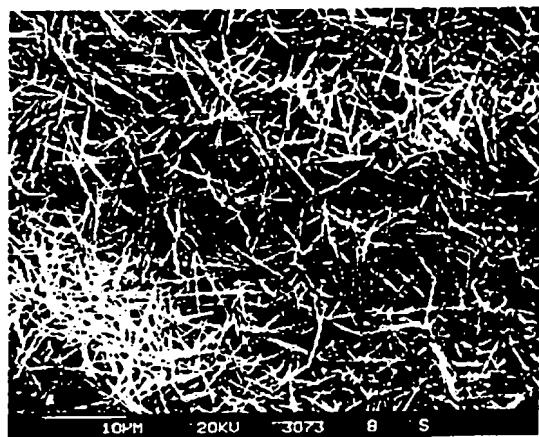


FIG 17



19/21

FIG 18

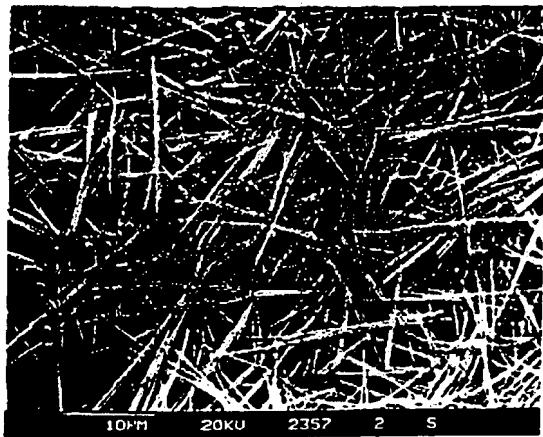


FIG 19

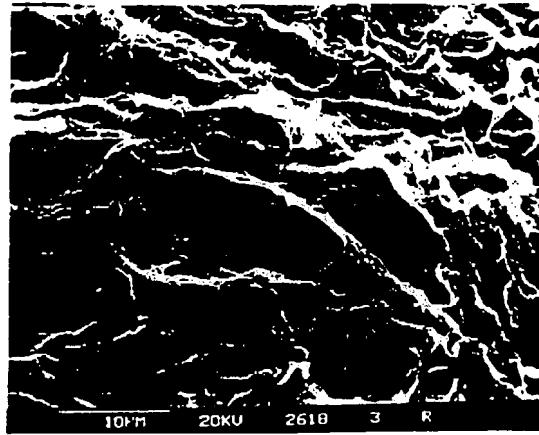


FIG 20

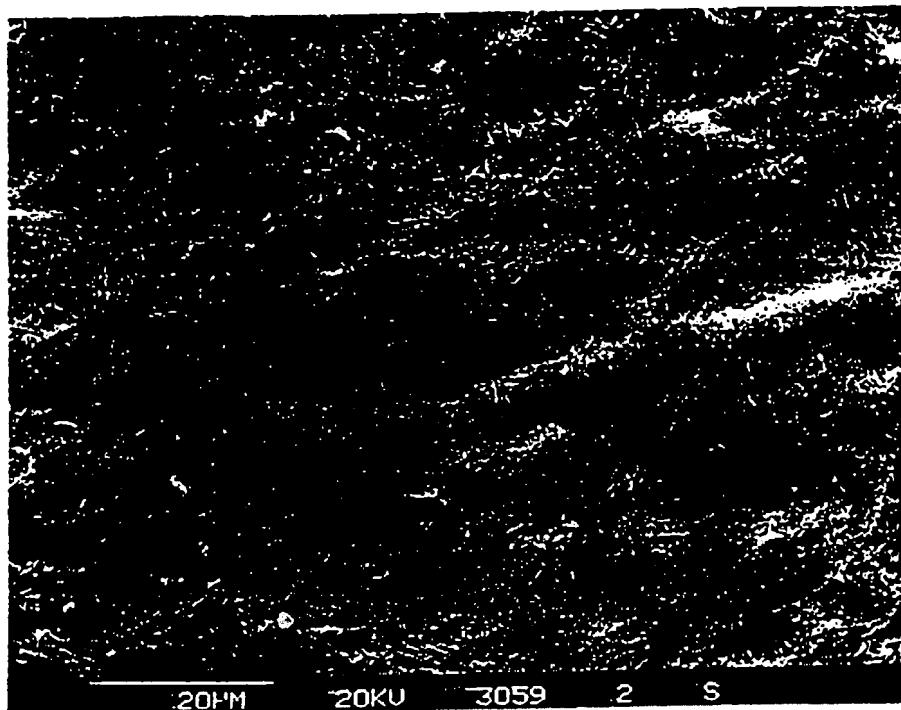
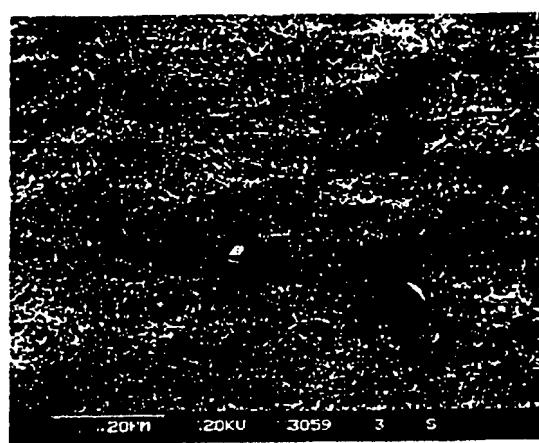


FIG 21



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NZ 95/00105

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C01B 33/24, 33/32, D21H 13/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : Int. Cl. ⁶ C01B 33/24, 33/32, D21H 13/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 3804652 (LAIDLER et al) 16 April 1974. See abstract, Fig 2, Example 1	1, 2, 6-9, 15-18, 21-24, 26-27, 31-34
A	Derwent Abstracts Accession No. 81-12903D/08, class E33, JP,A, 55-162421 (TOKUYAMA SODA KK) 17 December 1980. See whole abstract	1-34
A	Derwent Abstracts Accession No. 88-158548/23, class E33, JP,A, 63-099397 (TOKUYAMA SODA KK) 30 April 1988. See whole abstract	1-34

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
21 February 1996

Date of mailing of the international search report

29 Feb 1996

Name and mailing address of the ISA/AU
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA Facsimile No.: (06) 285 3929

Authorized officer

GRAEME BROXAM

Telephone No.: (06) 283 2133

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NZ 95/00105

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstracts Accession No. 88-094935/14, class E33, JP,A, 63-045115 (TOKUYAMA SODA KK) 26 February 1988. See whole abstract	1-34
A	Derwent Abstracts Accession No. 83-315706/60, class E33, SU,A, 1159884 (AS. ARMN. GEN. INORGAN.) 7 June 1985. See whole abstract	1-34
A	Derwent Abstracts Accession No. 81-431250/24, class E33, JP,A, 56-045818 (ASAHI CHEMICAL IND. KK) 25 April 1981. See whole abstract	1-34
A	EP,A, 0005992 (TURNER & NEWALL LIMITED) 12 December 1979. See abstract	1-34
A	DE,A, 3306478 (LUCHTRATH) 12 July 1984. See page 7 lines 20-36	1-34

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/NZ 95/00105

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	3804652	GB	1221060				
EP	47745/79	AU	47745/79	BR	7903476	DK	2324/79
		ES	481190	FI	791757	GB	2025383
		JP	55020291	NO	791812	ZA	7902643
DE	3306478	AU	23499/84	EP	131010	FI	843205
		IT	1194528	WO	8402710		